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Respectfully submitted,

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

00203744.8

Der Präsident des Europäischen Patentamts;
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5 PROCESS FOR IMPROVING THE PURITY OF QUATERNARY AMMONIUM HYDROXIDES BY ELECTROLYSIS

The present invention relates to a process for improving the purity of a composition comprising a quaternary ammonium hydroxide.

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Quaternary ammonium hydroxides such as tetramethylammonium hydroxide (TMAH) are used *inter alia* as a developer for photoresists in the manufacture of printed circuit boards and microelectronic chips and as a base in the production of 4-aminodiphenylamine (4-ADPA). Alkylated derivatives of 4-

15 ADPA such as N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) are used as an antidegradant in rubber compositions and rubber articles such as tyres.

In said production of 4-ADPA, the base (typically a quaternary ammonium hydroxide) - which is in the form of an aqueous solution - is recycled many times (hereinafter also referred to as recycle base). However, after a certain number of reaction cycles, the active content of the aqueous base solution has decreased to such an extent that it can no longer be used in the production process and either some of the recycle aqueous base solution is purged and 25 replaced with fresh base solution or all of it is discarded as waste, which adds to the cost of the 4-ADPA and 6PPD. Also, with an increasing number of reaction cycles, the liquid-liquid separation of the aqueous base solution from the 4-ADPA-containing organic phase proceeds with greater difficulty.

When TMAH has been used as the base, the purged/discardred aqueous base 30 solution contains *inter alia* various tetramethylammonium (TMA) salts, such as tetramethylammonium acetate, formate, chloride, carbonate, and oxalate, and

aniline – one of the starting materials for preparing 4-ADPA. It further contains small amounts of various other salts and other organic impurities.

The present invention provides a solution to these problems.

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Quaternary ammonium hydroxides are typically prepared by means of electrolysis. For example, TMAH is prepared from tetramethylammonium chloride using a two-compartment electrolysis cell comprising an anolyte compartment containing an anode and a catholyte compartment containing a cathode, said compartments being separated by a cation selective membrane. Said membrane is also referred to in the art as a cation-exchange membrane.

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It is also known in the art to improve the purity of mixtures comprising quaternary ammonium hydroxides by electrolysis.

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For example, US 4,714,530 discloses a process for producing high-purity quaternary ammonium hydroxides by means of electrolysis using a two-compartment electrolysis cell equipped with a cation-exchange membrane in which an aqueous solution containing the quaternary ammonium hydroxide is charged to the anolyte compartment.

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US 5,389,211 discloses a process for improving the purity of organic or inorganic hydroxides such as quaternary ammonium hydroxides by means of electrolysis using an electrolysis cell comprising at least one intermediate compartment which is separated from the anolyte and catholyte compartments by at least two nonionic dividers and/or cation selective membranes. The mixture containing the hydroxide is charged to the anolyte compartment. It is mentioned that the catholyte and intermediate compartments may also contain organic or inorganic hydroxide prior to initiation of the electrolysis. The purpose

of charging purified hydroxide to the intermediate compartment is to avoid the build-up of impurities in that compartment (col. 12, ll. 47-51).

The processes of US 4,714,530 and US 5,389,211 relate to improving the 5 purity of in particular aqueous solutions of quaternary ammonium hydroxides which have been used as a developer for photoresists in printed circuit boards and microelectronic chips, which solutions typically contain significant amounts of halogen. The waste aqueous solutions comprising quaternary ammonium hydroxides which are obtained during the production of 4-ADPA, however, 10 generally do not have a similarly high halogen content.

It was found that the electrolysis of recycle TMAH – obtained from the production of 4-ADPA – by charging it to the anolyte compartment of a two-compartment electrolysis cell soon after its start resulted in the formation of a 15 significant amount of a solid material at the anode, which fouled the electrode and virtually stopped the electrolysis (see Examples).

Surprisingly, it was subsequently found that the formation of the solid material at the anode could be prevented if the electrolysis was carried out in accordance with the present invention.

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The process for improving the purity of a composition comprising a quaternary ammonium hydroxide in accordance with the present invention comprises the steps of

- (a) providing an electrolysis cell which comprises an anolyte compartment 25 containing an anode, a catholyte compartment containing a cathode, and at least one intermediate compartment, said at least one intermediate compartment being separated from the anolyte and catholyte compartments by cation selective membranes,
- (b) charging water, optionally containing a supporting electrolyte, to the 30 anolyte compartment, charging water, optionally containing a quaternary

ammonium hydroxide, to the catholyte compartment, and charging a composition comprising the quaternary ammonium hydroxide to be purified to the intermediate compartment,

(c) passing a current through the electrolysis cell to produce a purified aqueous quaternary ammonium hydroxide solution in the catholyte compartment, and

(d) recovering the purified aqueous quaternary ammonium hydroxide solution from the catholyte compartment.

10 In the case of recycle base which is obtained from the production of 4-ADPA, the invention process results in the recovery from the catholyte compartment of an aqueous solution containing lower amounts of anions, such as acetate, formate, chloride, carbonate, and oxalate, than are present in the recycle base and, if desired, having a higher quaternary ammonium hydroxide content. The 15 recovered aqueous solution further contains a portion of the neutral organic compounds such as aniline which are present in the recycle base.

Due to the fact that the anolyte and catholyte compartments contain aqueous solutions, oxygen gas is formed at the anode and hydrogen gas is formed at 20 the cathode. The presence of tetramethylammonium carbonate and/or tetramethylammonium bicarbonate in the intermediate compartment may cause the formation of carbon dioxide gas, which depends on the pH of the solution in the intermediate compartment. These gases are handled and processed in a conventional way.

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The invention process can be carried out using any known electrolysis cell equipped with conventional electrodes and cation selective membranes, said electrodes and membranes being compatible with the solutions which are charged to and formed in the anolyte, intermediate, and catholyte 30 compartments, in a way known to the person skilled in this art.

The anode and the cathode may be made from a variety of materials. The anode must be suitable for oxygen formation/evolution and the cathode for hydrogen formation/evolution. The cathode may also be an oxygen reducing/oxygen depolarized cathode. Preferably, a dimensionally stable anode (DSA) for oxygen evolution and a stainless steel cathode are used.

The cation selective membranes may be any which are used in the electrolysis of quaternary ammonium salts to quaternary ammonium hydroxides and the electrolytic purification of quaternary ammonium hydroxides. A distinction is made between perfluorinated and non-perfluorinated membranes. Preferably, the cation selective membranes are perfluorinated membranes, for example made from polytetrafluoroethylene, such as the ones sold under the name Nafion (from DuPont). Other suitable cation selective membranes include membranes made from polyethylene, polypropylene, polyvinylchloride, polystyrene-divinylbenzene, and (sulfonated) polysulfone.

Apart from the fact that cation selective membranes allow the passage of cations and prevent the transport of anions, said membranes are also selective for the type of cation. For example, in the art proton selective membranes are known.

In the invention process, at least two cation selective membranes are used. These membranes may be identical or not. Preferably, the invention process is carried out using a proton selective membrane, separating the anolyte compartment from the intermediate compartment, and a membrane selective for the quaternary ammonium ion which is present in the composition comprising the quaternary ammonium hydroxide to be purified, separating the intermediate compartment from the catholyte compartment.

The electrolysis cell to be used in the invention process contains at least one intermediate compartment. Hence, the cell contains three or more compartments, the compartments each being separated by cation selective membranes as described above. Preferably, a three-compartment electrolysis cell is used, since the use of more than two cation selective membranes increases the cost of the electrolysis cell as well as the consumption of electricity. Generally, the inclusion of additional cation selective membranes will result in an increase in the purity of the aqueous quaternary ammonium hydroxide solution recovered from the catholyte compartment.

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If a high-purity aqueous quaternary ammonium hydroxide solution is desired and consequently two or more intermediate compartments are used, in accordance with the invention process the composition comprising the quaternary ammonium hydroxide to be purified is charged to that intermediate compartment which is immediately next to the anolyte compartment. In that case, the other intermediate compartment(s) and catholyte compartment typically will contain aqueous quaternary ammonium hydroxide solutions of high purity, e.g., of the desired purity.

20 The quaternary ammonium hydroxide-containing compositions which are purified in accordance with the process of the present invention typically are aqueous solutions containing from 1 to 45, preferably 5 to 40, more preferably 10 to 35 wt% of quaternary ammonium hydroxide. These compositions may however further contain an organic solvent.

25 It was found to be advantageous to dilute the recycle base obtained from the production of 4-ADPA before charging it to the intermediate compartment.

30 The quaternary ammonium hydroxide-containing composition to be used in the process of the present invention may contain any quaternary ammonium hydroxide, typically the composition comprises a tetrahydrocarboxylammonium

hydroxide or hydrocarbylene di(trihydrocarbyl)ammonium dihydroxide. Typical examples include tetramethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, choline hydroxide, phenyltrimethylammonium hydroxide, benzyltrimethylammonium hydroxide, and 5 bis-dibutylethyl hexamethylene diammonium hydroxide (hexamethylene 1,6-di(dibutylethyl)ammonium dihydroxide). Other suitable examples have been described in the prior art cited above, i.e. US 4,714,530 (col. 2, I. 60 through col. 3, I. 2) and US 5,389,211 (col. 5, II. 43-60). Preferably, the composition comprises tetramethylammonium hydroxide (TMAH).

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At the start of electrolysis, the anolyte compartment contains water, optionally containing a supporting electrolyte, and the catholyte compartment contains water, optionally containing a quaternary ammonium hydroxide. The term "supporting electrolyte" is known to the person skilled in this art. The supporting electrolyte is present mainly to increase the conductivity of the anolyte solution. In the catholyte compartment, the increase in conductivity of the catholyte solution is performed by including a quaternary ammonium hydroxide. The presence of electrolytes in the anolyte and catholyte compartments allows current to flow through the electrolysis cell immediately after the start of the electrolysis. It is to be noted that it is not critical to the invention process which electrolyte-containing aqueous solutions are present in the anolyte and catholyte compartments. Their choice will mainly be determined by the desired purity and the desired active content of the aqueous quaternary ammonium hydroxide solution to be recovered from the catholyte compartment. 20 Preferably, dimineralized or soft water is used in the invention process.

25 Preferably, the anolyte solution contains a supporting electrolyte. Preferably, the anolyte compartment contains an aqueous solution of a strong acid such as sulfuric acid or phosphoric acid, preferably sulfuric acid. A practical anolyte solution to start with is an aqueous 1 to 10, preferably 3 to 9, more preferably 3 30

to 5 wt% sulfuric acid solution. Preferably, the volume (i.e. water is consumed during the electrolysis and transported towards the catholyte compartment), the active content, and the level of impurities in the aqueous solution present in the anolyte compartment are monitored, and the volume and the active content are adjusted if necessary. If the level of impurities becomes undesirably high, the entire anolyte solution may be discarded and replaced with a fresh solution.

Preferably, the catholyte compartment contains an aqueous solution of a quaternary ammonium hydroxide which is the same as the quaternary ammonium hydroxide present in the composition to be purified. Generally, the catholyte solution is an aqueous 1 to 45, preferably 5 to 40, more preferably 10 to 35 wt% solution of the quaternary ammonium hydroxide. Preferably, the catholyte compartment is charged with an aqueous quaternary ammonium hydroxide solution of high purity, e.g., a solution having the desired purity. The active content may vary as desired.

As mentioned before, the composition comprising the quaternary ammonium hydroxide to be purified is charged to the intermediate compartment. If more than one intermediate compartment is used, it preferably is charged to the compartment bordering the anolyte compartment.

Preferably, the invention process is carried out by charging a batch of the composition comprising the quaternary ammonium hydroxide to be purified to the intermediate compartment and continuing the electrolysis until practically all of the quaternary ammonium ions are removed therefrom before charging a subsequent batch to the intermediate compartment. The processed batch - present in the intermediate compartment - may either be discarded wholly or partly and is then replaced by or mixed with the subsequent batch, respectively.

The electrolysis of the composition comprising the quaternary ammonium hydroxide is effected by applying a direct current between the anode and the

cathode with a current density of generally up to $4,000 \text{ A/m}^2$. A practical range is from 500 to $1,500 \text{ A/m}^2$. The current is applied to the electrolysis cell for a period of time sufficient to allow for the transport of preferably all quaternary ammonium ions from the intermediate compartment to the catholyte compartment. An important parameter for monitoring the progress of the invention process is the pH of the solution in the intermediate compartment to which the composition to be purified has been charged.

During the electrolysis of the composition comprising the quaternary ammonium hydroxide to be purified, the pH of the solution of the intermediate compartment decreases due to the transport of protons from the anolyte compartment to the intermediate compartment and the transport of quaternary ammonium ions from the intermediate compartment to the catholyte compartment. Anions such as chloride ions are unable to pass the cation selective membrane separating the intermediate compartment from the catholyte compartment. A weak acid such as acetic acid, however, is able to pass a cation selective membrane by way of diffusion. Preferably, the electrolysis is stopped once a pH of 1 to 7, more preferably 4 to 7, even more preferably 4 to 6, most preferably about 5 is reached in the intermediate compartment.

In the case of recycle base obtained from the production of 4-ADPA, if the invention process is carried out batchwise, the pH in the intermediate compartment drops from a value of higher than 10 to any desired final pH value. If only a part of the processed composition - present in the intermediate compartment - is replaced by a subsequent batch the pH may be maintained between certain chosen values, e.g., between 5 and 7.

Typically, the aqueous solutions present in each of the compartments of the electrolysis cell are circulated by means of pumping.

During the electrolysis, the temperature of the solutions within the compartments typically is maintained at from 10 to 90, preferably 40 to 80, more preferably 40 to 60, most preferably 40 to 50°C.

5. The present invention is illustrated by the following Examples.

Examples 1 and 2

10

Two experiments were performed using a three-compartment Micro Flow Cell (from ElectroCell) comprising an anolyte compartment containing an anode, a catholyte compartment containing a cathode, and an intermediate compartment being separated from the anolyte and catholyte compartments by two cation 15 selective membranes. EPDM gaskets and Teflon frames were used.

In the first experiment, i.e., Example 1, two Nafion 117 membranes (from DuPont) were used. The anode at the start of the experiment was platinum, later it was replaced with a dimensionally stable anode (DSA) for oxygen 20 evolution (both from ElectroCell). The cathode was stainless steel (from ElectroCell). The anolyte solution was changed several times as a result of which on average it contained 2.17 wt% aqueous H_2SO_4 and 4.59 wt% aqueous acetic acid (HAc) and the amount of tetramethylammonium (TMA)-acetate in the intermediate compartment increased. The starting catholyte 25 solution was 6.7 wt% aqueous tetramethylammonium hydroxide (TMAH). The recycle base contained 12.85 wt% TMAH and was charged to the intermediate compartment of the electrolysis cell.

In the second experiment, i.e., Example 2, two Nafion 324 membranes were 30 used. The anode was a DSA for oxygen evolution, the cathode stainless steel.

The anolyte was 2.50 wt% aqueous H₂SO₄, the catholyte was 4.94 wt% aqueous TMAH. The recycle base contained 19.90 wt% TMAH and was charged to the intermediate compartment.

The results depicted in Tables 1-3 show that the electrolysis of recycle TMAH results in a considerable purification of the base in that the amounts of TMA-acetate, TMA-formate, TMA-chloride, TMA₂-carbonate, and TMA₂-oxalate in the aqueous solution recovered from the catholyte compartment are considerably lower than in the solution present in the intermediate compartment, and that the TMAH content in the aqueous solution that is recovered from the catholyte compartment has increased notably while leaving no TMAH in the intermediate compartment. Additionally, some aniline is present in the aqueous solution which is recovered from the catholyte compartment.

The detection limits are as follows: TMA-acetate (0.0023 wt%), TMA-formate (0.0013 wt%), TMA-chloride (0.0015 wt%), TMA₂-carbonate (0.0350 wt%), TMA₂-oxalate (0.0027 wt%), and TMAH (0.0100 wt%).

Table 1. Electrolysis data

Example	1	2
Average current efficiency (%)	32	60
Average current density (A/m ²)	700	450
Temperature (°C)	45	45
Final pH intermediate compartment	5.2	1.1
DC Voltage (V)	7	7.5

Table 2. Starting and recovered base compositions

Example 1		A _{start}	A _{final}	I _{start}	I _{final}	C _{start}	C _{final}
TMA-Acetate	wt%			0.86	4.44	nd	0.06
TMA-Formate	wt%			1.34	1.05	nd	0.04
TMA-Chloride	wt%			0.03	0.003	nd	0.002
TMA ₂ -Carbonate	wt%			11.55	0.61	nd	0.49
TMA ₂ -Oxalate	wt%			2.05	1.58	nd	0.02
TMAH	wt%			12.85	nm	6.7	24.0
Aniline	wt%			1.33	0.35	nd	0.59
H ₂ SO ₄	wt%	2.17					
HAc	wt%	4.59					
Weight	g	3536.8	3030.9	832.6	722.7	726.8	765.2
Samples taken	g				179.2		164.9

A_{start} is the starting solution in the anolyte compartment, A_{final} is the final anolyte solution, I_{start} is the starting solution in the intermediate compartment, I_{final} is the final solution in the intermediate compartment, C_{start} is the starting catholyte solution, and C_{final} is the final catholyte solution, TMA represents tetramethylammonium, nm means not measurable (below the detection limit), nd means not determined.

Table 3. Starting and recovered base compositions

Example 2		A _{start}	A _{final}	I _{start}	I _{final}	C _{start}	C _{final}
TMA-Acetate	wt%			1.23	1.45	nd	0.05
TMA-Formate	wt%			0.83	1.00	nd	0.08
TMA-Chloride	wt%			0.02	0.003	nd	0.002
TMA ₂ -Carbonate	wt%			9.65	0.64	nd	0.23
TMA ₂ -Oxalate	wt%			1.55	2.05	nd	0.02
TMAH	wt%			19.90	nm	4.94	25.6
Aniline	wt%			2.68	nd	nd	nd
H ₂ SO ₄	wt%	2.50	3.03				
Weight	g	790.6	408.2	932.6	438.2	607.2	954.1
Water added	g	50.7		323.0			
Samples taken	g		213.0		318.9		186.2

A_{start} is the starting solution in the anolyte compartment, A_{final} is the final anolyte solution, I_{start} is the starting solution in the intermediate compartment, I_{final} is the final solution in the intermediate compartment, C_{start} is the starting catholyte solution, and

C_{final} is the final catholyte solution, TMA represents tetramethylammonium, nm means not measurable (below the detection limit), nd means not determined.

Comparative Examples A and B

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Two experiments were performed using a two-compartment Micro Flow Cell (from ElectroCell) comprising an anolyte compartment containing an anode and a catholyte compartment containing a cathode, said compartments being separated by means of a cation selective membrane. EPDM gaskets and

10 Teflon frames were used.

In the first experiment, i.e. Comparative Example A, a Nafion 450 membrane was used. The anode was a platinum electrode, the cathode stainless steel. The recycle base was charged to the anolyte compartment and it contained

15 13.61 wt% TMAH. The starting catholyte solution was 13.85 wt% aqueous TMAH.

In the second experiment, i.e. Comparative Example B, a Nafion 117 membrane was used. The anode was a DSA for oxygen evolution, the cathode 20 stainless steel. The recycle base was charged to the anolyte compartment and it contained 12.68 wt% TMAH, the catholyte was 12.09 wt% aqueous TMAH.

The results of these experiments are shown in Tables 4 to 6.

It was found that at the anode a significant amount of a solid material was 25 formed which fouled the electrode and had to be removed periodically in order to be able to continue the electrolysis. Ultimately, the electrolysis virtually stopped (TMA bound to carbonate was not transported from the anolyte to the catholyte compartment). As a result, the electrolysis could not be performed long enough for an economically attractive recovery of TMAH to be obtained. In 30 addition, the removal of this solid was time consuming and cumbersome.

Table 4. Electrolysis data

Comparative Example	A	B
Average current efficiency (%)	35	19
Average current density (A/m ²)	1300	2400
Temperature (°C)	46	47
DC Voltage (V)	7.7	8.2

Table 5. Starting and recovered base compositions

Comp. Ex. A		A _{start}	A _{final}	C _{start}	C _{final}
TMA-Acetate	wt%	0.74	0.66	nm	nm
TMA-Formate	wt%	1.09	1.02	nm	nm
TMA-Chloride	wt%	0.02	0.02	nm	nm
TMA ₂ -Carbonate	wt%	12.08	18.18	0.16	0.32
TMA ₂ -Oxalate	wt%	1.89	1.43	nm	nm
TMAH	wt%	13.61	0.33	13.85	21.98
Aniline	wt%	1.90	0.44	nd	0.24
Weight	g	900	830	750	420
Water added	g	100			
Samples taken	g		240		240

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A_{start} is the starting anolyte solution, A_{final} is the final anolyte solution,

C_{start} is the starting catholyte solution, and C_{final} is the final catholyte solution,

nm means not measurable (below the detection limit), nd means not determined.

Table 6. Starting and recovered base compositions

Comp. Ex. B		A_{start}	A_{final}	C_{start}	C_{final}
TMA-Acetate	wt%	0.67	1.08	nm	nm
TMA-Formate	wt%	1.06	1.25	nm	nm
TMA-Chloride	wt%	0.02	0.02	nm	nm
TMA ₂ -Carbonate	wt%	13.25	24.98	nm	nm
TMA ₂ -Oxalate	wt%	1.86	1.65	nm	nm
TMAH	wt%	12.68	nm	12.09	23.44
Aniline	wt%	1.79	0.56	nd	0.47
Weight	g	900	570	750	530
Water added	g	100			
Samples taken	g		120		120

A_{start} is the starting anolyte solution, A_{final} is the final anolyte solution,

C_{start} is the starting catholyte solution, and C_{final} is the final catholyte solution,

5 nm means not measurable (below the detection limit), nd means not determined.

CLAIMS

1. A process for improving the purity of a composition comprising a quaternary ammonium hydroxide comprising the steps of

5 (a) providing an electrolysis cell which comprises an anolyte compartment containing an anode, a catholyte compartment containing a cathode, and at least one intermediate compartment, said at least one intermediate compartment being separated from the anolyte and catholyte compartments by cation selective membranes,

10 (b) charging water, optionally containing a supporting electrolyte, to the anolyte compartment, charging water, optionally containing a quaternary ammonium hydroxide, to the catholyte compartment, and charging a composition comprising the quaternary ammonium hydroxide to be purified to the intermediate compartment,

15 (c) passing a current through the electrolysis cell to produce a purified aqueous quaternary ammonium hydroxide solution in the catholyte compartment, and

(d) recovering the purified aqueous quaternary ammonium hydroxide solution from the catholyte compartment.

20 2. A process according to claim 1, characterized in that the anolyte compartment in step (b) contains an aqueous solution of a strong acid, preferably sulfuric acid.

25 3. A process according to claim 2, characterized in that the anolyte compartment contains an aqueous 1 to 10 wt% sulfuric acid solution.

4. A process according to any one of the preceding claims, characterized in that the catholyte compartment in step (b) contains an aqueous solution of a quaternary ammonium hydroxide which is the same as the quaternary ammonium hydroxide present in the composition to be purified.
5. A process according to any one of the preceding claims, characterized in that the quaternary ammonium hydroxide is tetramethylammonium hydroxide (TMAH).
10 6. A process according to claim 4 or 5, characterized in that the catholyte compartment contains an aqueous 5 to 40 wt% TMAH solution.
7. A process according to any one of the preceding claims, characterized in that a three-compartment electrolysis cell is used.
15 8. A process according to any one of the preceding claims, characterized in that the electrolysis is stopped once a pH of 1 to 7 is reached in the intermediate compartment.
20 9. A process according to claim 8, characterized in that the electrolysis is stopped once a pH of 4 to 7 is reached in the intermediate compartment.
10. A process according to any one of the preceding claims, characterized in that the cation selective membranes are perfluorinated membranes.

ABSTRACT

The present invention relates to a process for improving the purity of a composition comprising a quaternary ammonium hydroxide comprising the 5 steps of (a) providing an electrolysis cell which comprises an anolyte compartment containing an anode, a catholyte compartment containing a cathode, and at least one intermediate compartment, said at least one intermediate compartment being separated from the anolyte and catholyte compartments by cation selective membranes, (b) charging water, optionally 10 containing a supporting electrolyte, to the anolyte compartment, charging water, optionally containing a quaternary ammonium hydroxide, to the catholyte compartment, and charging a composition comprising the quaternary ammonium hydroxide to be purified to the intermediate compartment, (c) passing a current through the electrolysis cell to produce a purified aqueous 15 quaternary ammonium hydroxide solution in the catholyte compartment, and (d) recovering the purified aqueous quaternary ammonium hydroxide solution from the catholyte compartment. The process is particularly suitable for improving the purity of aqueous solutions of tetramethylammonium hydroxide which has been recycled many times during the preparation of 4-aminodiphenylamine.